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WO 97/14400

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**COSMETIC COMPOSITION FOR THE TREATMENT OF KERATINOUS MATERIALS  
 COMPRISING AT LEAST ONE GRAFTED SILICONE POLYMER AND AT  
 LEAST ONE AQUEOUS DISPERSION OF INSOLUBLE PARTICLES OF  
 NONIONIC OR CATIONIC POLYMER**

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**Abstract**

The present invention relates to a cosmetic or dermatological composition for the treatment of keratinous materials, particularly hair, comprising in a cosmetically or dermatologically acceptable medium at least a grafted silicone polymer with a polysiloxanic skeleton grafted by organic non silicone monomers and at least an aqueous dispersion of insoluble particles of non ionic or cationic polymer. The compositions of the invention are used particularly as rinsed products or as non rinsed products particularly for hair washing, hair care, hair conditioning, hair dressing or hair setting.

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The present invention relates to a cosmetic or dermatological composition for the treatment of keratinous materials, particularly hair, comprising at least one grafted silicone polymer, with a polysiloxane backbone grafted with nonsilicone organic monomers and at least one aqueous dispersion of insoluble nonionic or cationic polymer particles.

It has been proposed to use aqueous dispersions of insoluble polymer particles in hair care compositions.

However, until now, the obtained results have not been satisfactory. Indeed, the fixing power is not yet sufficient, the drying time is too long, and the cosmetic properties are not yet satisfactory. In addition, when washing the hair with a shampoo, elimination of the polymer is difficult.

The state of the art also contains known polymers with a polysiloxane backbone grafted with nonsilicone organic monomers. They are preferably chosen from those described in the applications EP-A-0582152 and WO 93/23009. They are used, in particular, in capillaire compositions for their hair styling properties.

The compositions for hair washing and/or care and/or treatment containing in their formulations hair dressing polymers of this type generally present the drawback of presenting a fixing power which is still insufficient.

The term "fixing power of the composition" denotes the ability of the latter to impart to hair a cohesiveness which is such that the initial shaping of the hair is preserved.

Thus, one seeks compositions that do not present the drawbacks described above.

The applicant has discovered, surprisingly, that by combining at least one silicone polymer with a polysiloxane backbone grafted with nonsilicone organic monomers with at least one dispersion of insoluble particles of a nonionic or cationic polymer, the above mentioned drawbacks were overcome.

These compositions present a good fixing power and good cosmetic properties, such as untangling and hair styling or hair brushing after application, as well as softness, touchability and smoothness of the hair.

The composition according to the invention is thus essentially characterized by the fact that it comprises, in a cosmetically or dermatologically acceptable medium, at least one grafted silicone polymer, with a polysiloxane backbone grafted with nonsilicone organic monomers and at least one dispersion of insoluble nonionic or cationic polymer particles.

Below, the term "silicone polymer" is used, in agreement with the general accepted meaning, to denote all organosilicone polymers or oligomers with a linear or cyclic, branched or crosslinked structure, having a variable molecular weight, obtained by the polymerization and/or

polycondensation of appropriately functionalized silanes, and consisting essentially of the repetition of principal units in which the silicon atoms are bound to each other by oxygen atoms (siloxane bond  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ), optionally substituted hydrocarbon radicals that are directly connected by means of a carbon atom to said silicon atoms. The most routinely used hydrocarbon radicals are alkyl radicals, notably C<sub>1</sub>-C<sub>10</sub> alkyl radicals, in particular methyl, fluoroalkyl radicals, aryl radicals, in particular phenyl, alkenyl radicals, in particular vinyl; other types of radicals that are capable of being bonded either directly or by means of a hydrocarbon radical to the siloxane chain are, notably, hydrogen, halogens, in particular chlorine, bromine or fluorine, thiols, alkoxy radicals, polyoxyalkylene (or polyether) radicals, in particular, polyoxyethylene and/or polyoxypropylene, hydroxyl or hydroxyalkyl radicals, substituted or unsubstituted amino groups, amide groups, alkyloxy or alkyloxyalkyl radicals, hydroxyalkylamino or aminoalkyl radicals, quaternary ammonium groups, amphoteric or betaine groups, anionic groups, such as carboxylates, thioglycolates, sulfosuccinates, thiosulfates, phosphates and sulfates, where this list is naturally in no way limiting (so called "organo-modified" silicones).

According to the present invention, the grafted silicone polymer(s) which must be used are those which comprise a principal silicone (or polysiloxane ( $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ )<sub>n</sub>) chain, onto which is grafted, inside said chain as well as optionally at least one of its ends, at least one organic group that does not contain silicone.

These silicone polymers can be existing commercial products, or they can be obtained according to any means known to a person skilled in the art, particularly by a reaction between (i) a starting silicone correctly functionalized on one or more of these silicon atoms, and (ii) a nonsilicone organic compound which itself is correctly functionalized by a function which is capable of reacting with the functional group(s) borne by said silicone, by forming a covalent bond; a conventional example of such a reaction is the hydrosilylation reaction between  $\equiv\text{Si}-\text{H}$  groups and vinyl groups CH<sub>2</sub>=CH-, or the reaction between thio functional groups, -SH with these same vinyl groups.

Examples of silicone polymers that are suitable for the implementation of the present invention, as well as their particular preparation procedure, are notably described in the Patent Applications EP-A-0582 152, WO 93/23009 and WO 95/03776, whose teachings are included in their entirety in the present description as nonlimiting references.

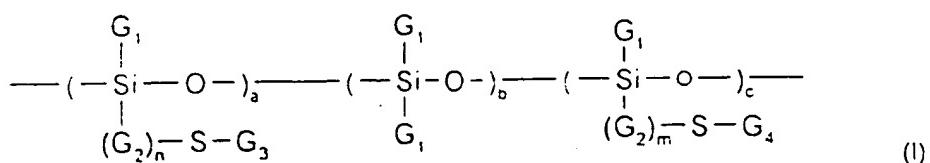
According to a particularly preferred embodiment of the present invention, the silicone polymer used comprises the result of radical polymerization between, on the one hand, at least one nonsilicone, anionic ethylenically unsaturated organic monomer and/or one nonsilicone, hydrophobic ethylenically unsaturated organic monomer and, on the other hand, a silicone presenting, in its chain, at least one functional group capable of reacting with said ethylenic

unsaturations of said nonsilicone monomers by forming a covalent bond, in particular thio functional groups.

According to the present invention, said ethylenically unsaturated anionic monomers are preferably chosen, alone or in a mixture, from linear or branched unsaturated carboxylic acids, which may optionally be partially or completely neutralized in the form of a salt, where these unsaturated carboxylic acids can be, more specifically, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid. The suitable salts are, notably, alkali, alkaline earth and ammonium salts. It should be noted, similarly, that in the final grafted silicone polymer, the organic group with anionic character which comprises the results of the radical (homo)polymerization of at least one anionic monomer of the unsaturated carboxylic acid type can be post-neutralized with a base (sodium hydroxide, ammonia ...) after the reaction, to convert it to the form of a salt.

According to the present invention, the ethylenically unsaturated hydrophobic monomers are preferably chosen, alone or in a mixture, from the alkanol acrylic acid esters and/or alkanol methacrylic acid esters. The alkanols are preferably C<sub>1</sub>-C<sub>18</sub>, more specifically, C<sub>1</sub>-C<sub>12</sub>. The preferred monomers are chosen from the group consisting of isoctyl (meth)acrylate, isononyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isopentyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, tert-butyl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate or mixtures thereof.

A family of grafted silicone polymers that is particularly well suited for the implementation of the present invention consists of the silicone polymers comprising in their structure the following unit having formula (I):



in which the radicals G<sub>1</sub>, which may be identical or different, represent hydrogen or a C<sub>1</sub>-C<sub>10</sub> alkyl radical, or a phenyl radical; the radicals G<sub>2</sub>, which may be identical or different, represent a C<sub>1</sub>-C<sub>10</sub> alkylene group; G<sub>3</sub> represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer; G<sub>4</sub> represents a polymeric residue resulting from the (homo)polymerization of at least one monomer of at least one ethylenically unsaturated hydrophobic monomer; m and n are equal to 0 or 1; a is a whole number from 0 to 50; b is a whole number that can be between 10 and 350, c is a whole number from 0 to 50; with the reservation that one of the parameters a and c must be different from 0.

It is preferred for the unit having formula (I) above to present at least one, and even more advantageously, all of the following characteristics:

- the radicals  $G_1$  denote an alkyl radical, preferably the methyl radical;
- n is not equal to zero, and the radicals  $G_2$  represent a divalent  $C_1$ - $C_3$  radical, preferably a propylene radical;
- $G_3$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the ethylenically unsaturated carboxylic acid type, preferably acrylic acid and/or methacrylic acid;
- $G_4$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the  $C_1$ - $C_{10}$  alkyl (meth)acrylate type, preferably of the isobutyl or methyl (meth)acrylate type.

Examples of silicone polymers having formula (I) are, notably, polydimethylsiloxanes (PDMS) to which are grafted, by means of a connection chain of the thiopropylene type, mixed polymer units of the poly(meth)acrylic acid type or of the methyl poly(meth)acrylate type. Other examples of silicone polymers having formula (I) are, notably, polydimethylsiloxanes (PDMS) to which are grafted, by means of a connection chain of the thiopropylene type, polymer units of the isobutyl poly(meth)acrylate type.

It is preferred for the number-average molecular weight of the silicone polymers of the invention to vary between approximately 10,000 and 1,000,000, and even more advantageously between approximately 10,000 and 100,000.

The grafted silicone polymers according to the invention are preferably used in a quantity ranging from 0.01 to 20 wt% of the total weight of the composition. More advantageously, this quantity varies from 0.1 to 15 wt%, and even more specifically from 0.5 to 10 wt%.

The aqueous dispersions of insoluble nonionic or cationic polymer particles that can be used according to the invention are generally obtained by polymerization or suspension or emulsion copolymerization of monomers according to the well known methods of the state of the art (such dispersions are also known under the name of "latex"). One can also obtain aqueous dispersions of polymers by dissolving said polymer in a water miscible organic solvent, followed by the addition of water, and finally the evaporation of the organic solvent. This type of preparation is described, for example, in French Patent Application No. 2 697 160.

The mean diameter of the insoluble polymer particles is generally less than 500 nm, and preferably less than 250 nm. Generally, the glass transition temperature is between -30°C and 90°C, and preferably it is between 10 and 35°C.

The polymer of the aqueous dispersion comprises at least one monomer chosen, for example, from styrene, butadiene, ethylene, tetrafluoroethylene, propylene, vinyltoluene, vinyl propionate, vinyl alcohol, acrylonitrile, chloroprene, vinyl chloride, vinyl acetate, urethanes,

isoprene, isobutene and the esters or amides of acrylic or methacrylic acid, maleic, crotonic or itaconic acid, the vinyl ethers, vinylpyrrolidone, vinylimidazole, trimethylammonioethyl (meth)acrylate and mixtures thereof.

The aqueous dispersions which can be used according to the invention can originate from the condensation of ionic or nonionic monomers that produce nonionic or cationic polymers such as, for example, polyesters, polyamides, polyurethanes or polyethers.

The nonionic polymers in the aqueous dispersions which can be used according to the invention are chosen, for example, from the following compounds:

- the homopolymers of vinyl acetate, such as the product available under the name of APPRETAN EM from the company HOECHST or the product available under the name of RHODOPAS A 012 from the company RHÔNE POULENC;

- the copolymers of vinyl acetate and acrylic ester, such as the product available under the name of RHODOPAS AD 310 from RHÔNE POULENC;

- the copolymers of vinyl acetate and ethylene, such as the product available under the name of APPRETAN TV from the company HOECHST;

- the copolymers of vinyl acetate and maleic ester, for example, dibutyl maleate, such as the product available under the name of APPRETAN MB EXTRA from the company HOECHST;

- the homopolymers of vinyl chloride such as the products available under the names of GEON 460X45, GEON 460X46 and GEON 577 from the company GOODRICH;

- polyethylene waxes, such as the products available under the names of AQUACER 513 and QAUACER 533 from the company BYK CERA;

- polyethylene/polytetrafluoroethylene waxes such as the products available under the names of DREWAX D-3750 from the company DREW AMEROID and WAX DISPERSION WD-1077 from the company R.T. NEWELL;

- the copolymers of polyethylene and maleic anhydride;

- the homopolymers of alkyl acrylates and the homopolymers of alkyl methacrylates, such as the product available under the name of MICROPEARL RQ 750 from the company MATSUMOTO or the product available under the name of LUHYDRAN A 848 S from the company BASF;

- the copolymers of acrylic esters, such as, for example, the copolymers of alkyl acrylates and alkyl methacrylates such as the products available from the company ROHM & HAAS under the names of PRIMAL ACZ 61 k and EUDRAGIT NE 30 D, from the company BASF under the names of ACRONAL 601, LUHYDRAW LR 8833 or 8845, from the company HOECHST under the names of APPRETAN N 9213 or N9212;

- the copolymers of acrylonitrile and of a nonionic monomer chosen, for example, from butadiene and alkyl (meth)acrylates; one can mention the products available under the names of NIPOLEX 531 B from the company NIPPON ZEON or those available under the name of CJ 0601 B from the company ROHM & HAAS;

- the homopolymers of styrene, such as the product RHODOPAS 5051 available from the company RHÔNE POULENC;

- the copolymers of styrene and of alkyl (meth)acrylate such as the products MOWILITH LDM 6911, MOWILITH DM 611 and MOWILITH LDM 6070 available from the company HOECHST, the products RHODOPAS SD 215 and RHODOPAS DS 910 available from the company RHÔNE POULENC, the product URAMUL SC 70 available from the company DSM;

- the copolymers of styrene, alkyl methacrylate and alkyl acrylate such as the product DAITISOL SPA available from the company WACKHERR;

- the copolymers of styrene and of butadiene such as the products RHODOPAS SB 153 and RHODOPAS SB 012 available from the company RHÔNE POULENC;

- the copolymers of styrene, butadiene and vinylpyridine, such as the products GOODRITE SB VINYL PYRIDINE 2528X10 and GOODRITE SB VINYL PYRIDINE 2508 available from the company GOODRICH:

- the copolymers of styrene and vinylpyrrolidone, such as the products ANTARA 450 and CLOUD 285 available from the company ISP;

- the polyurethanes such as the products available under the names of ACRYSOL RM 1020 or ACRYSOL RM 2020 from the company ROHM & HAAS, such as the products URAFLEX XP 401 UZ, URAFLEX XP 402 UZ from the company DSM RESINS;

- the copolymers of alkyl acrylate and urethane such as the product 8538-33 from the company NATIONAL STARCH;

- the polyamides such as the product ESTAPOR LO 11 available from the company RHÔNE POULENC.

The dispersions of insoluble cationic polymer particles comprise, for example, the following polymers:

- the copolymers of acrylamide and of trimethylammonioethyl (meth)acrylate;

- the copolymers of alkyl methacrylate, alkyl acrylate and trimethylammonioethyl (meth)acrylate, such as the product EUDRAGIT RL 30 D available from the company ROHM PHARMA.

The aqueous dispersions of insoluble polymer particles that are particularly preferred in the context of the invention are the aqueous dispersions of nonionic insoluble polymer particles.

The concentration by weight of the insoluble polymer particles in the compositions according to the invention is preferably between 0.1 and 50 wt% with respect to the total weight of the composition and preferably between 1 and 30 wt%.

The cosmetically or dermatologically acceptable medium preferably consists of water or a mixture of water and cosmetically acceptable solvents, such as monoalcohols, polyalcohols, glycol ethers or fatty acid esters, which can be used alone or in a mixture.

More specifically, one can mention lower alcohols, such as ethanol, isopropanol, polyalcohols such as diethylene glycol, glycol ethers, glycol alkyl ethers or diethylene glycol alkyl ethers.

The grafted silicone polymers according to the invention can be dissolved in said cosmetically acceptable medium or used in the form of an aqueous dispersion of insoluble particles.

The composition of the invention can also contain at least one additive chosen from thickeners, fatty acid esters, fatty acid and glycerol esters, volatile silicones, surfactants, perfumes, preservatives, sunscreens, proteins, vitamins, polymers, plant, animal, mineral or synthetic oils, or any other additive conventionally used in the cosmetics field.

These additives are present in the composition according to the invention in proportions that can range from 0 to 20 wt% with respect to the total weight of the composition. The precise quantity of each additive is a function of its type and it is easily determined by a person skilled in the art.

Naturally, a person skilled in the art will ensure that the optional compound(s) to be added to the composition according to the invention is (are) chosen in such a manner that the advantageous properties intrinsically associated with the composition according to the invention are not, or not substantially, altered by the addition considered.

The compositions according to the invention can be in the form of a gel, milk, cream, lotion having a variable degree of thickness, or foam.

The compositions according to the invention are used as rinsed products or as nonrinsed products, notably for washing, caring for, conditioning, maintaining or shaping keratinous substances, such as hair.

More specifically, they are hair styling products, such as perming lotions, brushing lotions, fixing compositions (lacquers) and hair dressing compositions. The lotions can be packaged in various forms, notably in sprayers, pump bottles or in aerosol containers to ensure application of the composition in spray form or in the form of a foam. Such packaging forms are indicated, for example, when one wishes to obtain a spray, lacquer or foam for use in fixing or treating hair.

The compositions can also be shampoos, rinse or nonrinse compositions, to be applied before or after shampooing, dyeing, bleaching, perming or untangling.

When the composition according to the invention is packaged in the form of an aerosol to obtain a lacquer or an aerosol foam, it comprises at least one propellant which can be chosen from volatile hydrocarbons, such as n-butane, propane, isobutane, pentane, a chlorinated and/or fluorinated hydrocarbon and mixtures thereof. One can also use, as the propellant, carbon dioxide, nitrogen monoxide, dimethyl ether, nitrogen, compressed air and mixtures thereof.

The invention also relates to a method for the treatment of keratinous substances such as hair, which consists in applying to the hair a composition as defined above, optionally followed by rinsing with water.

The invention will now be illustrated more completely with the help of the following examples which should not be considered to limit the invention to the described embodiments. In the following, AI denotes active ingredient.

#### Example 1 Aerosol hair dressing spray

- Grafted silicone polymer having formula (I) and a polymethyl/methylsiloxane structure with propyl-3-thiopolymethacrylic acid groups and propyl 3-thio methyl polymethacrylate groups	3 g
- Homopolymer of vinyl acetate in an aqueous dispersion with 50% of AI available under the name of APPRETAN EM from the company HOECHST	4 g AI
- Aminomethylpropanol qsp	
100% neutralization of the grafted silicone polymer	
- Dimethyl ether	30 g
- Water	qsp 100 g

The composition is pressurized in an aerosol.

This composition was applied to dry hair: the hair presented a good feel, good maintenance and a good hold over time.

The composition is easily eliminated with shampooing.

#### Example 2 Hair dressing spray in an aerosol

- Grafted silicone polymer having formula (I) having a polymethyl/methylsiloxane structure with propyl-3-thiopolymethacrylic acid groups and propyl-3-thiomethyl polymethacrylate groups	4 g
- Copolymer of styrene and butadiene in an aqueous dispersion at 50% of AI available under the name RHODOPAS SB 012	

from the company RHÔNE POULENC		2 g AI
- Aminomethylpropanol qsp		
100% neutralization of the grafted silicone polymer		
- Dimethyl ether		30 g
- Water	qsp	100 g

The composition is pressurized in an aerosol.

This composition was applied to dry hair: the hair presented a good feel, good maintenance and a good hold over time.

The composition is easily eliminated with shampooing.

### Claims

1. Cosmetic or dermatological composition intended for the treatment of keratinous materials, characterized by the fact that it comprises, in a cosmetically or dermatologically acceptable medium at least one grafted silicone polymer, with a polysiloxane backbone grafted with nonsilicone organic monomers and at least one aqueous dispersion of insoluble nonionic or cationic polymer particles.

2. Composition according to Claim 1, characterized by the fact that the grafted silicone polymer comprises a principal chain of polysiloxane onto which is grafted, inside said chain as well as optionally to at least one of its ends, at least one organic group containing no silicone.

3. Composition according to Claim 1 or 2, characterized by the fact that the grafted silicone polymer can be obtained by radical copolymerization between, on the one hand, at least one ethylenically unsaturated nonsilicone anionic organic monomer and/or one ethylenically unsaturated nonsilicone hydrophobic organic monomer, and on the other hand, a polysiloxane presenting in its chain at least one, and preferably more, functional groups capable of reacting with said ethylenically unsaturated bonds of said nonsilicone monomers.

4. Composition according to Claim 3, characterized by the fact that the ethylenically unsaturated anionic organic monomer is chosen, alone or in the form of a mixture of monomers, from linear or branched unsaturated carboxylic acids.

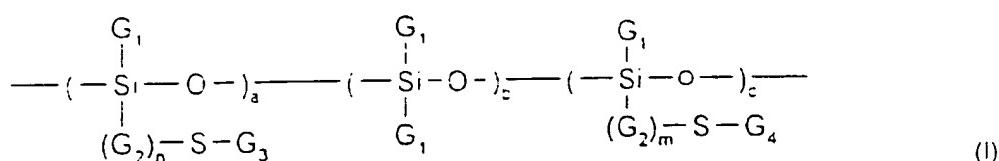
5. Composition according to Claim 4, characterized by the fact that the ethylenically unsaturated anionic organic monomer is chosen, alone or in the form of a mixture of monomers, from acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid and their alkali, alkaline earth or ammonium salts, or mixtures thereof.

6. Composition according to Claim 3, characterized by the fact that the ethylenically unsaturated hydrophobic organic monomer is chosen, alone or in a mixture of monomers, from alkanol acrylic acid esters and/or alkanol methacrylic acid esters, the alkanol being preferably C<sub>1</sub>-C<sub>18</sub> alkanol.

7. Composition according to Claim 6, characterized by the fact that the ethylenically unsaturated hydrophobic organic monomer is chosen, alone or in a mixture of monomers, from the group consisting of isoctyl (meth)acrylate, isononyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isopentyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, tert-butyl (meth)acrylate, tridecyl (meth)acrylate, and stearyl (meth)acrylate.

8. Composition according to any one of Claims 1-7, characterized by the fact that the grafted silicone polymer comprises on the principal silicone chain, at least one organic group with anionic character obtained by radical (homo)polymerization of at least one anionic monomer of the carboxylic acid type, either partially unsaturated or completely neutralized in the form of a salt.

9. Composition according to any one of Claims 1-8, characterized by the fact that the grafted silicone polymer is chosen from the silicone polymers comprising in their structure the following formula unit (I):



in which the radicals  $\text{G}_1$ , which may be identical or different, represent hydrogen or a  $\text{C}_1\text{-C}_{10}$  alkyl radical, or a phenyl radical; the radicals  $\text{G}_2$ , which may be identical or different, represent a  $\text{C}_1\text{-C}_{10}$  alkylene group;  $\text{G}_3$  represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer;  $\text{G}_4$  represents a polymeric residue resulting from the (homo)polymerization of at least one monomer of at least one ethylenically unsaturated hydrophobic monomer;  $n$  and  $m$  are equal to 0 or 1;  $a$  is a whole number from 0 to 50;  $b$  is a whole number that can be between 10 and 350,  $c$  is a whole number from 0 to 50; with the reservation that one of the parameters  $a$  and  $c$  must be different from 0.

10. Composition according to Claim 9, characterized by the fact that the formula unit (I) presents at least one of the following characteristics:

- the radicals  $\text{G}_1$  denote a  $\text{C}_1\text{-C}_{10}$  alkyl radical;
- $n$  is not equal to zero, and the radicals  $\text{G}_2$  represent a divalent  $\text{C}_1\text{-C}_3$  radical;
- $\text{G}_3$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the ethylenically unsaturated carboxylic acid type;

-  $G_4$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the  $C_1-C_{10}$  alkyl (meth)acrylate type.

11. Composition according to Claim 9 or 10, characterized by the fact that the formula unit (I) simultaneously presents the following characteristics:

- the radicals  $G_1$  denote a methyl radical;

- n is not equal to zero, and the radicals  $G_2$  represent a propylene radical;

- $G_3$  represents a polymer radical resulting from the (homo)polymerization of at least one acrylic acid and/or methacrylic acid;

- $G_4$  represents a polymer radical resulting from the (homo)polymerization of at least one methyl (meth)acrylate.

12. Composition according to any one of Claims 1-11, characterized by the fact that the number-average molecular weight of the grafted silicone polymer is in the approximate range of 10,000-1,000,000, and more preferably approximately 10,000-100,000.

13. Composition according to any one of the preceding claims, characterized by the fact that the grafted silicone polymer(s) are present at concentrations of 0.01-20 wt% with respect to the total weight of the composition, preferably 0.1-15 wt%, and more particularly 0.5-10 wt%.

14. Composition according to any one of the preceding claims, characterized by the fact that the polymer of the aqueous dispersion comprises at least one monomer chosen from styrene, butadiene, ethylene, propylene, vinyltoluene, vinyl propionate, vinyl alcohol, acrylonitrile, chloroprene, vinyl acetate, the urethanes, isoprene, isobutene and esters or amides of acrylic or methacrylic acid, maleic acid, crotonic or itaconic acid, vinyl ether, vinylpyrrolidone, vinylimidazole, trimethylammonioethyl (meth)acrylate and mixtures thereof.

15. Composition according to any one of the preceding claims, characterized by the fact that the nonionic polymer of the aqueous dispersion is chosen from polyesters, polyamides, polyurethanes and polyethers.

16. Composition according to any one of the preceding claims, characterized by the fact that the nonionic polymer of the aqueous dispersions is chosen from:

- vinyl acetate homopolymers;

- copolymers of vinyl acetate and acrylic ester;

- copolymers of vinyl acetate and ethylene;

- copolymers of vinyl acetate and maleic acid;

- vinyl chloride homopolymers;

- polyethylene waxes;

- polyethylene/polytetrafluoroethylene waxes;

- copolymers of polyethylene and maleic anhydride;

- alkyl acrylate homopolymers and alkyl methacrylate homopolymers;

- acrylic ester copolymers, such as, for example, copolymers of alkyl acrylates and alkyl methacrylates:

- copolymers of acrylonitrile and a nonionic monomer chosen, for example, from butadiene and alkyl (meth)acrylates:

- styrene homopolymers;

- copolymers of styrene and alkyl (meth)acrylate;

- copolymers of styrene, alkyl methacrylate and alkyl acrylate;

- copolymers of styrene and butadiene;

- copolymers of styrene, butadiene and vinylpyridine;

- copolymers of styrene and vinylpyrrolidone; and

- copolymers of alkyl acrylate and urethane.

17. Composition according to any one of Claims 1-14, characterized by the fact that the cationic polymer of the aqueous dispersion is chosen from:

- copolymers of acrylamide and trimethylammonioethyl (meth)acrylate;

- the copolymers of alkyl methacrylate, alkyl acrylate and trimethylammonioethyl (meth)acrylate.

18. Composition according to any one of the preceding claims, characterized by the fact that the concentration by weight of the insoluble polymer particles is 0.1-50% with respect to the total weight of the composition.

19. Composition according to any one of the preceding claims, characterized by the fact that the concentration by weight of the insoluble polymer particles is 1-30% with respect to the total weight of the composition.

20. Composition according to any one of the preceding claims, characterized by the fact that it contains in addition at least one additive chosen from the group consisting of thickeners, fatty acid esters, esters of fatty acids and glycerol, silicones, surfactants, perfumes, preservatives, sunscreens, proteins, vitamins, polymers, plant, animal, mineral or synthetic oils, or any other additive conventionally used in the cosmetics field.

21. Composition according to any one of the preceding claims, characterized by the fact that the cosmetically or dermatologically acceptable medium consists of water or a mixture of water and at least one cosmetically acceptable solvent.

22. Composition according to Claim 21, characterized by the fact that the cosmetically acceptable solvents are chosen from the group consisting of monoalcohols, polyalcohols, glycol ethers, fatty acid esters and mixtures thereof.

23. Composition according to any one of the preceding claims, characterized by the fact that the keratinous material is hair.

24. Composition according to any one of the preceding claims, characterized by the fact that it is in the form of a gel, milk, cream, lotion of a varying degree of thickness, or foam.

25. Composition according to any one of Claims 1-24, characterized by the fact that it is a hair styling product.

26. Composition according to any one of Claims 1-25, characterized by the fact that it is a hair care product chosen from the group of shampoos; rinse or nonrinse hair care products to be applied before or after a shampoo, dyes, bleaches, styling [gels], or straighteners.

27. Composition according to any one of Claims 1-26, characterized by the fact that it is packaged in the form of a sprayer, pump bottle or in an aerosol container to obtain a spray, a lacquer or a foam.

28. Composition according to any one of the preceding claims, characterized by the fact that the grafted silicone polymer is dissolved in the cosmetically or dermatologically acceptable medium or used in the form of an aqueous dispersion of insoluble particles.

29. Nontherapeutic method for the treatment of keratinous substances, particularly hair, characterized by the fact that it consists in applying to said materials a composition as defined in any one of Claims 1-28, optionally followed by rinsing with water.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/FR 96/01570

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Description of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 95 03776 A (MINNESOTA MINING &amp; MANUFACTURING) 9 February 1995</p> <p>cited in the application</p> <p>see page 33, line 9-13; claims 1-9, 11-13, 16-18, 30</p> <p>see page 37, line 13</p> <p>see page 37, line 26 - line 36</p> <p>see page 41, line 29 - line 31</p> <p>see page 47, line 9 - line 15</p> <p>see page 47, line 32 - line 36</p> <p>see page 48, line 1 - line 5</p> <p>see page 33, line 9 - line 13</p> <p>-----</p>	1-16, 18-29

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- '&' document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**International Application No  
PCT/FR 96/01570

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9503776	09-02-95	US-A- 5468477 EP-A- 0714275	21-11-95 05-06-96